

# Effects and Control of Steam in the Systems of Methanol and DME Synthesis from Syngas over Cu-based Catalysts

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**Abstract** Effects of steam in the systems of methanol synthesis over  $\text{CuZnOAl}_2\text{O}_3$  catalyst and one-step DME synthesis over  $\text{CuZnOAl}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3\text{-HZSM-5}$  were investigated, respectively. The results showed that there were two different effects in both systems: for the former (methanol synthesis), a little steam (<10%) in the feed gas increased the catalytic activity and stability; for the latter (DME synthesis) where steam was created significantly, presence of steam in the feed gas accelerated sintering of Cu particles and deactivation velocity. The results of hydro-thermal treatment of pre-reduced  $\text{CuZnOAl}_2\text{O}_3$  catalyst showed that high temperature (>240 °C) and high steam content (>10%) can greatly enhance the sintering velocity of Cu crystalline. Commercial nano- $\text{SiO}_2$  and nano- $\text{Al}_2\text{O}_3$  with high surface area were utilized to control the steam concentration in the system of one-step DME synthesis. Owing to their hydrophilic surface, however, neither of them depressed the deactivation velocity effectively. The pre-treatment of nano- $\text{SiO}_2$  support with alcohol can change the surface of the support from hydrophilic to hydrophobic property, which can be found to control the steam surrounding the active metallic Cu and keep the catalytic stability.

**Keywords** Steam · Methanol · DME synthesis · Syngas · Nano-silica · Alcohol pre-treatment

## 1 Introduction

DME, as a clean alternative fuel for diesel engines, has certain advantages over methanol for the valorization of alternative resources to oil via syngas. DME is a relatively inert compound, non-corrosive for metals and it is not carcinogenic. Its toxicity is much lower than that of methanol. Its physical properties are similar to those of LPG so it can be distributed, stored and used as a LPG substitute. In addition, DME is also being used as an aerosol propellant to replace chlorofluoro carbons, which are found to destroy the ozone layer of the atmosphere [1].

In the single-step process of DME synthesis from syngas, CO conversion is higher than that of single methanol synthesis due to the continuous dehydration. So direct synthesis of DME from synthesis gas in a single reactor with hybrid catalyst has being attracted many researchers and industrial attention at the present time [2–6]. As is all known, the process of methanol synthesis from synthesis gas over  $\text{CuZnOAl}_2\text{O}_3$  catalysts has been commercialized since 1960s. While up to now, all commercial DME are produced by the dehydration of methanol and the process of one-step DME synthesis from syngas has not been industrialized yet. The main barriers for industrialization of direct DME synthesis process are the great deal of heat from catalyst bed and the significant content of steam and  $\text{CO}_2$  in the system, which accelerated the deactivation of Cu-based catalysts. Accordingly, the slurry-bed process for one-step DME synthesis from syngas was developed to overcome the hot-spot of catalyst bed and keep the catalytic stability [2, 7, 8]. However, this three-phase process was confronted with the issue of diffusion resistance and the difficulty of product separation, which restricted its application.

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The effects of steam and  $\text{CO}_2$  in the system of methanol synthesis over Cu-based catalysts were investigated by some researchers [9–11], who found that the steam in the system accelerated crystallization of Cu and ZnO, and the hydro-thermal conditions facilitated the sintering of Cu particles. According to this fact, Wu et al. [10] and Brands et al. [12] utilized colloidal silica and  $\text{SiO}_2$  support to suppress the crystallization, respectively. Compared to the methanol synthesis, the fix-bed process for one-step DME synthesis from syngas was more complex. Therefore, it is essential to discuss the effect of reaction system on catalytic activity and stability of Cu-based catalysts.

In this paper, the effects of steam on activity and stability of Cu-based catalysts have been contrasted between methanol synthesis and one-step DME synthesis. In addition, supports with high surface area have been utilized to regulate the steam content in the catalysts bed, so as to decrease the deactivation velocity of Cu-based catalysts.

## 2 Experimental

The catalyst for methanol synthesis  $\text{CuZnOAl}_2\text{O}_3$  (denoted as MeOHcat) was prepared in a co-precipitation method as follows: an aqueous solution of Cu, Zn and Al nitrate and a solution of  $\text{Na}_2\text{CO}_3$  were co-precipitated under vigorous stirring. The mole ratio of Cu/Zn/Al was 6:3:1, then it was stirred, filtered, dried and calcined. The catalyst for one-step DME synthesis  $\text{CuZnOAl}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3\text{-HZSM-5}$  (denoted as DMEcat) was prepared in a co-precipitation sedimentation method. After co-precipitation mentioned above, the slurry was filtered, washed and added to HZSM5 and  $\gamma\text{-Al}_2\text{O}_3$ , then it was stirred, filtered, dried and calcined.

The pre-treatment of nano-silica supports was as follows: 2.0 g silica was impregnated with ethanol and butanol at room temperature, respectively (denoted as Et- $\text{SiO}_2$  and Bu- $\text{SiO}_2$ ). Then they were dried overnight and calcined at 300 °C for 4 h.  $\text{SiO}_2$  + DMEcat and  $\text{Al}_2\text{O}_3$  + DMEcat (denoted as R-Si-DMEcat, Si-DMEcat and Al-DMEcat, respectively) were prepared in a mechanical mixing method with nano- $\text{SiO}_2$  (fresh and pre-treated) and nano- $\text{Al}_2\text{O}_3$ , respectively, where the nano-oxide supports covered 15wt%.

The methanol and DME synthesis reaction was carried out in a conventional fixed-bed flow reactor. The catalyst (1 mL, 20–40 mesh) was packed in a stainless-steel tube. The catalyst was re-reduced in situ with  $\text{H}_2$  under atmospheric pressure at 220 °C. The feed gas composition was  $\text{H}_2/\text{CO}/\text{N}_2$ : 30/15/1, with different contents of steam. Reaction conditions: 220 °C, 2.0 MPa, 4,000  $\text{h}^{-1}$ . The products were analyzed by on-line chromatography with TCD and FID, Helium as a carrier gas. In the

hydro-thermal treatment experiments, 1.0 g  $\text{CuZnOAl}_2\text{O}_3$  catalysts were reduced by  $\text{H}_2$  at 220 °C for 2 h, and then treated with different  $\text{H}_2\text{-H}_2\text{O}$  mixtures at different temperatures for 4 h.

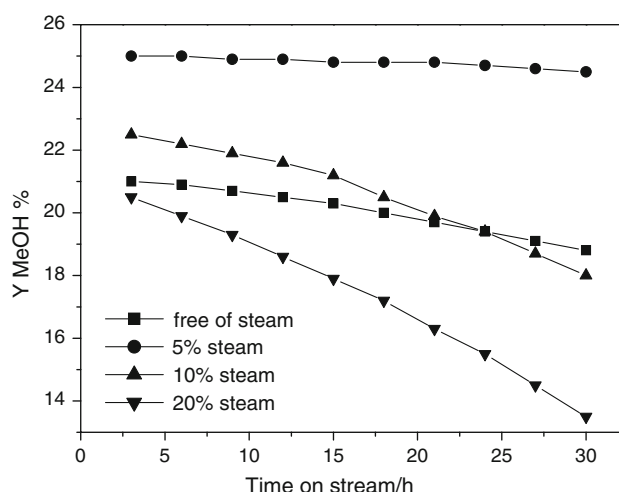
X-ray diffraction (XRD) data of catalysts were collected on a Rigaku Dmax-B diffract meter (CuK $\alpha$  radiation, 40 kV, 100 mA). The crystallite sizes of metallic Cu were evaluated from the full width at half maximum of the Cu (1 1 1) peaks by using the Scherrer equation.

The surface properties of the untreated and pre-treated silica supports were also analyzed by IR. The procedure for the IR measurements was as follows: the sample was first placed in the IR-reactor cell, and then purged with  $\text{N}_2$  at 383 K for 3 h to eliminate moisture. When the temperature was reduced to room temperature, the IR spectrum of the sample was recorded using air as the background.

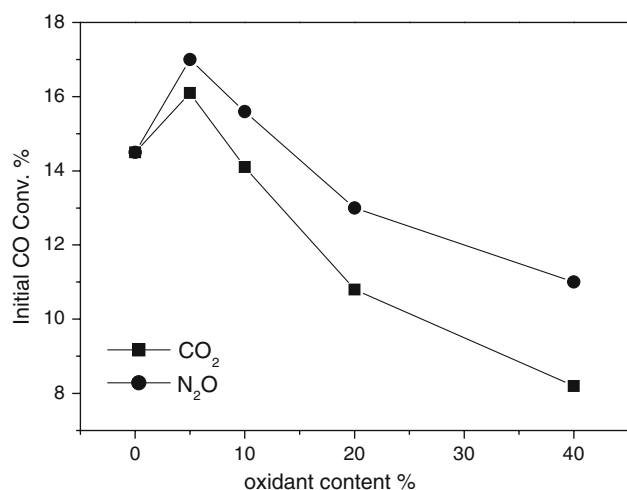
## 3 Results and Discussion

### 3.1 Effect of Steam for Methanol Synthesis

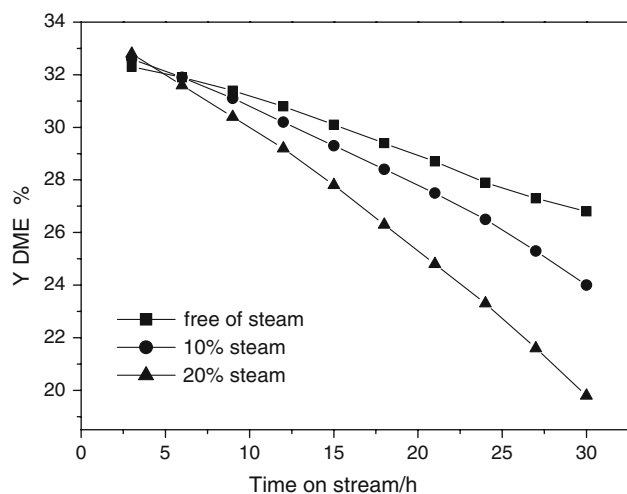
The effect of steam on catalytic activity and stability of  $\text{CuZnOAl}_2\text{O}_3$  catalysts for methanol synthesis is shown in Fig. 1. From this figure we can find that addition of small quantity (5%) of steam into the feed gas ( $\text{H}_2/\text{CO}$ ) improved activity and stability significantly. While with the increase of steam content, catalytic activity and stability declined rapidly. Especially for the feed with 20% steam, its deactivation velocity was more than three times higher than that from  $\text{H}_2/\text{CO}$ , in spite of their similar initial activity. Meanwhile, the effects of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  on the initial activity of  $\text{CuZnOAl}_2\text{O}_3$  catalysts for methanol synthesis are investigated in Fig. 2, respectively, from which it can be concluded that both of them ( $\text{CO}_2$  and  $\text{N}_2\text{O}$ ) have the



**Fig. 1** Effect of steam on methanol synthesis



**Fig. 2** Effect of CO<sub>2</sub> and N<sub>2</sub>O on methanol synthesis



**Fig. 3** Effect of steam on one-step DME synthesis

similar tendency with steam. That is to say, syngas (CO + H<sub>2</sub>) with a small amount of weakly oxidative atmosphere can obtain higher methanol yield over Cu-ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts. With the increase of oxidant addition (up to 10%), the yield of methanol keep decreasing.

Previous research of our group [13] showed that as active sites of methanol and DME synthesis, Cu<sup>0</sup>–Cu<sup>+</sup> was

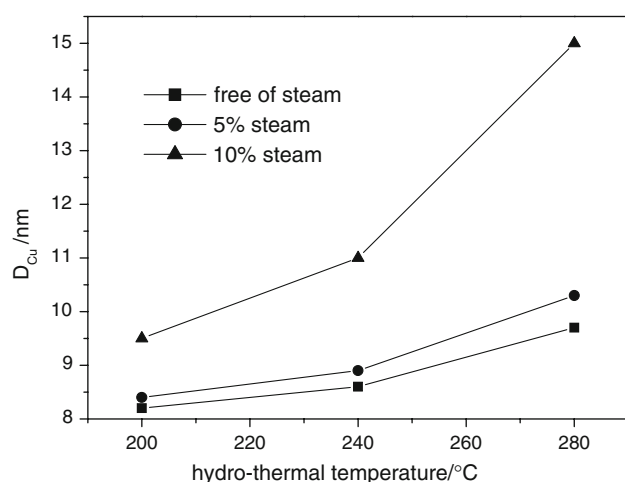
more active than Cu<sup>0</sup>. So the oxidative atmospheres were needed to some extent in the system to complete the cycle of Cu<sup>0</sup>–Cu<sup>+</sup>. Herein, N<sub>2</sub>O is usually served as a typical weakly oxidant which can oxidize surface metallic Cu to Cu<sup>+</sup> at low temperature [14]. Just like the role of N<sub>2</sub>O, it is suggested that in the system for methanol synthesis, either steam or CO<sub>2</sub> generated from WGS reaction which quickly reached equilibrium served as the oxidative atmospheres to regulate oxidation state of surface Cu species. In other words, when the steam content is 5%, the ratio of CO/CO<sub>2</sub> is about to match the optimum to keep the most active Cu species. Therefore, the promotional effect of steam is attributed to the ability to regulate oxidation state of active Cu species, rather than change the carbon source of methanol synthesis and other factors. The results agree well with that obtained by many researchers [11, 15] who found that addition of small count of CO<sub>2</sub> had improved the methanol yield. When the steam content is up to 20% the deactivation velocity increased greatly, which is probably due to the effect of steam on sintering of Cu particles. This will be discussed in details in Sect. 3.2.

### 3.2 Effect of Steam for One-Step DME Synthesis

Figure 3 and Table 1 depict the effect of steam on the one-step DME synthesis over DMEcat. Unlike the methanol synthesis from H<sub>2</sub>/CO, addition of small amount of (5%) steam gained almost the same reaction results as that from the steam-free feed gas (not shown). With the increase of steam content, the stability of Cu-based catalysts kept decreasing. It is shown in Table 1 that the decrease of DME yield is due to conversion of CO, rather than selectivity of DME. That is to say, deactivation of the catalysts is not from acid components, but from hydrogenation components. As is all known, there is significant content of steam or CO<sub>2</sub> in one-step DME synthesis system, where methanol synthesis reaction, methanol dehydration reaction and WGS reaction coexist. Therefore, feed gas with a small amount of steam gave no positive effects on DME synthesis reaction. From our previous experimental results [16, 17], including TPO, TPD and NH<sub>3</sub>-TPD, it is demonstrated that under our reaction conditions, the main

**Table 1** Reaction results of one-step DME synthesis over DMEcat, Si-DMEcat, Al-DMEcat and Bu-Si-DMEcat

		DMEcat	Si-DMEcat	Al-DMEcat	Bu-Si-DMEcat
$D_{Cu}/nm$	Initial	9.2	9.2	9.2	9.2
	After 50 h	13.6	12.3	12.5	9.9
Conv.CO %	Initial	43.9	41.8	39.6	39.4
	After 50 h	32.7	33.1	30.8	36.8
Sel <sub>DME</sub> %	Initial	71.2	69.7	72.9	68.3
	After 50 h	66.6	65.4	44.2	65.8



**Fig. 4** Effect of hydro-thermal treatment on Cu particles

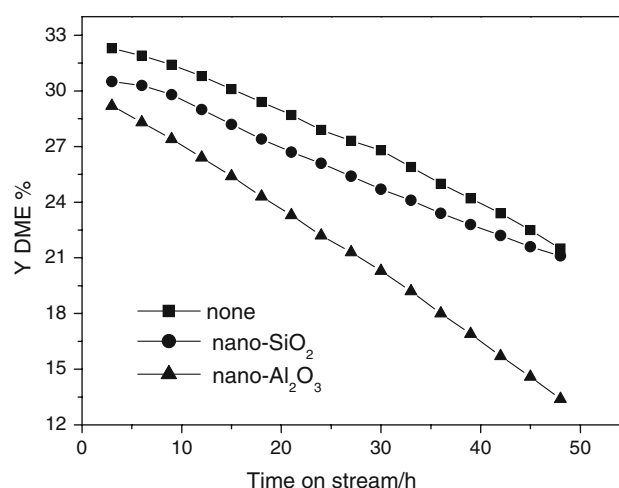
factor of the decrease of DME yield is the sintering of active Cu, rather than poisoning, coke deposition and the deactivation of dehydration component. So it is noteworthy to expect that addition of steam accelerated the deactivation of  $\text{CuZnOAl}_2\text{O}_3$  components, more probably, the sintering of Cu particles.

The hydro-thermal treatment experiments of reduced  $\text{CuZnOAl}_2\text{O}_3$  catalysts were designed to validate our suggestion, which is shown in Fig. 4. During hydro-thermal treatment metallic Cu in the catalysts had undergone crystallization to different extent. The changes of Cu crystal are affected by temperature and steam content. From this figure it can be seen that the temperature over 240 °C and the steam content over 10% will promote the Cu crystallization significantly, which confirms the suppose that addition of steam accelerated Cu sintering in the system of one-step DME synthesis.

Similarly to our results, Wu et al. [10] found that water (came from  $\text{CO}_2$  hydrogenation) in the system of methanol synthesis accelerated crystallization of Cu and ZnO whose particle size changed from ~8 to ~13 nm by XRD analysis. Likewise, Ladebeck [9] led to the conclusion from methanol synthesis that the copper crystallite growth rate by hydro-thermal treatment increased by a factor of 2.5 compared to that by thermal treatment alone. He also found that water in the system damaged the matrix material and probably decreased copper surface tension. What is mentioned above substantiates our suggestion in another way.

### 3.3 Control of Steam in the System of DME Synthesis

By comparing Figs. 1 and 3, we can see that even at the same condition and feed gas  $\text{CO}/\text{H}_2$ , the stability of one-step DME synthesis is much lower than that of methanol synthesis. According to what is mentioned above, we can



**Fig. 5** Effect of nano-supports on DME synthesis

attribute the fact mainly to the sintering of Cu crystallite at hydro-thermal atmospheres in the system of DME synthesis, which is one of the bottlenecks restraining one-step DME synthesis process for industrialization.

Nano-silica and nano-alumina, new materials with nano-scale regular porous system, abundant surface hydroxyl radicals and high surface area, are served as catalyst support and water absorbent. Brands et al. [12] found that during methanol synthesis, silica-supported Cu-based catalysts enhanced the stability against over-reduction and sintering of Cu species than co-precipitation catalysts. Similarly, in the work of Wu et al. [10], silica was introduced into the catalysts by adding colloidal silica into the aqueous solution of metal nitrates used for co-precipitation to suppress Cu and ZnO crystallization and improve the stability of catalysts. Therefore, it is supposed that addition of the new materials into one-step DME synthesis catalysts can enhance the stability by controlling the hot-spot of catalysts bed and reducing the steam content adjacent to the active Cu species.

The effects of nano-silica and nano-alumina on catalytic activity and stability for DME synthesis are shown in Fig. 5 and Table 1. Unexpectedly, from Fig. 5 we can apparently find that the effects of nano-silica and nano-alumina are rather unsatisfactory. Addition of the nano-SiO<sub>2</sub> improved catalytic stability insignificantly. Even worse, addition of nano-Al<sub>2</sub>O<sub>3</sub> accelerated the deactivation velocity. While from Table 1, we can discuss the difference between them in details. The addition of nano-scaled supports did not effectively suppress the sintering of Cu particles and keep the stability of catalysts. According to nano-Al<sub>2</sub>O<sub>3</sub>, however, the selectivity of DME decreased from 72.9% to 44.2%, which implied that the dehydration components, rather than hydrogenation components, deactivated rapidly. Clearly, the dehydration components

in the one-step DME synthesis catalysts need some acidity. Nevertheless, overmuch strong acid sites will help to producing long-chain hydrocarbons and coke deposition, which block the active sites and reduce the selectivity of DME [18, 19]. Silica has almost no acidity, while alumina has strong L-acid sites. Therefore, the addition of nano- $\text{Al}_2\text{O}_3$  will yield more hydrocarbons product and reduce the stability of DME synthesis evidently. According to what is mentioned above, nano-scaled supports with hydrophilic surface seem to be incapable of controlling the steam content in the catalyst bed and suppressing the sintering velocity of Cu.

There are many literatures concerning the modification of nano-silica support surface [20–22]. Qu et al. [20] found that during the calcination under some temperature, individual hydroxyl radicals on nano-silica surface could be partially eliminated. Fuji et al. [21] used alcohols (ROH) with different length of Alkyl to pre-treat nano-silica to change the surface property of silica. They found that after pre-treatment the hydroxyl radicals on the silica surface were replaced by alkoxy radicals (-OR) to some extent, and the silica supports were transformed from hydrophilic to hydrophobic surface, which was helpful to increase the dispersion of active metal.

Therefore, we pre-treated our nano-silica supports with ethanol (Et-silica), butanol (Bu-silica) and blank calcination (C-silica), respectively, in order to change the surface property of supports and depress the sintering velocity of Cu. The influence of support pre-treatment is shown in Fig. 6 and Table 1. From Fig. 6 we can see that (1) addition of calcined silica can suppress the deactivation velocity slightly; (2) addition of ethanol-pre-treated silica gave no significant change; interestingly, (3) addition of 1-butanol-pre-treated silica can suppress the deactivation

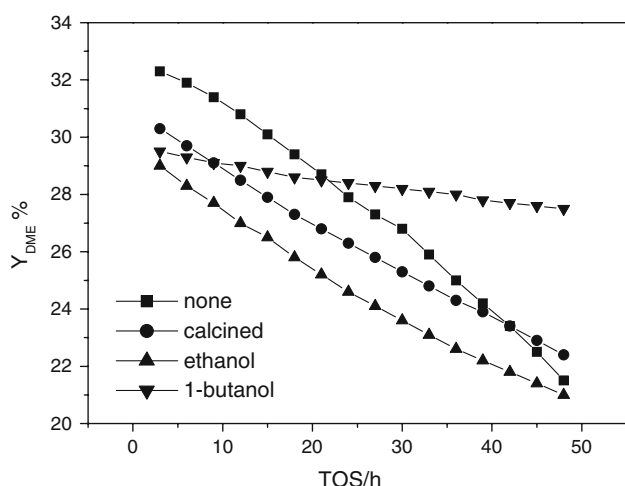


Fig. 6 Effect of pre-treatment of supports on DME synthesis

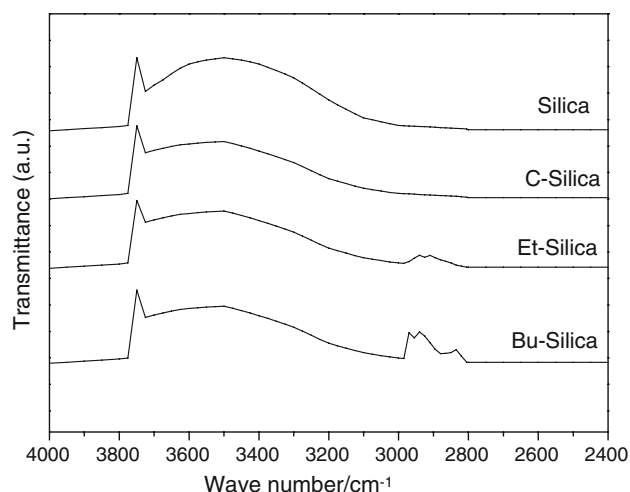


Fig. 7 FT-IR spectra of parent and pre-treated silica supports

velocity effectively, even though its initial activity decreased a little. In details, it can be found from Table 1 that the 1-butanol pre-treatment can depress the sintering velocity of Cu particles effectively. So Bu-Si-DMEcat kept rather stable CO conversion and DME selectivity. These results are well consistent with that obtained by Jiang [22], who found that during 1-butanol pre-treatment, silica surface was changed mostly (by IR spectrum) and the metallic Pd dispersion got the maximum relative to other alcohols.

To confirm the effect of pre-treatment of the silica supports, we investigated the surface properties of the different silica supports by FT-IR. As shown in Fig. 7, the sharp absorption band at  $3,743\text{ cm}^{-1}$  is assigned to isolated Si-OH stretching vibrations and the broad band between  $3,100$  and  $3,700\text{ cm}^{-1}$  to the hydrogen-bonded Si-OH stretching vibrations, while the absorption bands at ca.  $2,800\text{--}3,000\text{ cm}^{-1}$  correspond to C-H stretching vibrations of superficial alkoxy groups [23–26]. Comparing to the untreated silica support, there are obvious decrease in the densities of both the isolated Si-OH and the hydrogen-bonded Si-OH on the pre-treated silica supports, with the simultaneous appearance of the superficial alkoxy groups on the surface of Et-silica and Bu-silica. These results suggest that the alcohol molecules were grafted onto the silica surface by reacting with the Si-OH during the support pre-treatment. In addition, despite the similar densities of surface Si-OH, there was rather evident difference in the densities of superficial alkoxy groups between Et-silica and Bu-silica. It is suggested that the pre-treatment of silica support with butanol can form the hydrophobic surface of support. These results are consistent with that of catalytic stability for DME synthesis, which implies that the hydrophobic surface of catalysts contributed to control the steam content in the catalyst bed and inhibit the sintering velocity of Cu active sites.

#### 4 Conclusion

For the methanol synthesis reaction from CO/H<sub>2</sub> over CuZnOAl<sub>2</sub>O<sub>3</sub> catalyst, a little steam (<10%) in the feed gas increased the catalytic activity and stability. But in the one-step DME synthesis system, presence of steam in the feed gas accelerated sintering of Cu particles and deactivation velocity, which is attributed to the sintering of Cu particles in the hydro-thermal atmospheres. Commercial nano-SiO<sub>2</sub> and nano-Al<sub>2</sub>O<sub>3</sub> with high surface area were utilized to control the steam concentration in the catalytic bed of one-step DME synthesis. Owing to their hydrophilic surface, neither of them depressed the deactivation velocity significantly. The pre-treatment of nano-SiO<sub>2</sub> support with 1-butanol can change the surface of the support from hydrophilic to hydrophobic property, which can be used to control the steam surrounding the active Cu.

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